



**Applications of the iodine-iodide system
to
controlled potential coulometric determinations**

Ronald Karlsson

1975

Lund 1974



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41552412_0005

APPLICATIONS OF THE IODINE-IODIDE SYSTEM TO CONTROLLED
POTENTIAL COULOMETRIC DETERMINATIONS.

av

Ronald Karlsson

Fil.lic., Sm

Akademisk avhandling, som med vederbörligt tillstånd av
Matematisk-Naturvetenskapliga fakulteten vid universitetet
i Lund för vinnande av filosofie doktorsexamen kommer att
offentligen försvaras å Kemicentrum, Sölvegatan 39, hörsal
E, fredagen den 31 januari 1975, kl 10.15.



Applications of the iodine-iodide system
to
controlled potential coulometric determinations.

Ronald Karlsson, fil.lic., Sm.

1974

Analytisk kemi
Lunds Universitet



APPLICATIONS OF THE IODINE-IODIDE SYSTEM TO
CONTROLLED POTENTIAL COULOMETRIC DETERMINATIONS.

This review gives a summary and a discussion of the results from the following papers which will be referred to by the Roman numerals I-VIII.

- I Coulometric microdetermination of water,
Ronald Karlsson and K.J. Karrman,
Talanta, 1971, 18, 459.
- II Determination of small amounts of water with
coulometrically generated Karl Fischer reagent,
Ronald Karlsson,
Talanta, 1972, 19, 1639.
- III Solubility of water in benzene,
Ronald Karlsson,
J. Chem.Eng.Data, 1973, 18, 290.
- IV Coulometric microdetermination of carbon and
hydrogen in organic compounds,
Ronald Karlsson,
Mikrochim.Acta, in press.
- V A rapid automatic method for the determination
of oxygen in organic substances, using coulo-
metry at controlled potential,
K.J. Karrman and Ronald Karlsson,
Talanta, 1972, 19, 67.

- VI Controlled-potential iodometric titration
 of nitrite; Application to the determination
 of nitrite in meat products,
 Ronald Karlsson and Lars-Gunnar Torstensson,
 Talanta, 1974, 21, 945.
- VII Coulometric determination of dissolved oxygen
 in water,
 Ronald Karlsson and Lars-Gunnar Torstensson,
 Talanta, 1974, 21, 957.
- VIII Controlled potential iodometric determination
 of nitrate after reduction to nitrite by
 coppered cadmium,
 Ronald Karlsson and Lars-Gunnar Torstensson,
 Talanta, in press.

INTRODUCTION

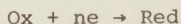
For more than a century it has been known that the extent of an electrode reaction is proportional to the quantity of electricity as expressed by Faraday's Law, but this relation was not exploited for analytical purposes until 1938. Szebelledy and Somogyi¹ were among the pioneers in this field and they coined the term coulometric analysis to designate the method of determining a substance in a solution by measuring the quantity of electricity required for its complete reaction in an electrolysis cell. The substance to be determined may directly undergo a reaction at one of the electrodes or it may react in the solution with another substance generated by one of the electrodes.

The quantity of the substance reacted is calculated via Faraday's Law from the measured quantity of electricity required. Hence the electrode reaction used in the coulometric analysis must in principle proceed with 100% current efficiency. The coulometric analysis is usually carried out either at constant current, originally devised by Szebelledy and Somogyi or at controlled potential, originally devised by Hickling². The papers in this thesis deal with coulometric analysis at controlled potential.

The fundamental principles for controlled potential coulometry according to Lingane³ are the following: The total E applied to an electrolysis cell can be written

$$E = E_C + E_A + iR$$

where E_C and E_A are the potentials of the cathode and anode, respectively, i is the current in amperes and R the resistance of the cell. A reduction at the cathode can be expressed



and the cathode potential is:

$$E_C = E_O + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} + \epsilon$$

where ϵ is the over-voltage. The anode reaction can be represented by a similar expression.

At the cathode the ratio $a_{\text{red}}/a_{\text{ox}}$ increases and the cathode potential tends to become more negative and similar considerations show that the anode potential tends to be more positive. Consequently, an increase in the back e.m.f.

$(E_C + E_A)$ is the net effect. The anode potential, E_A , can be maintained relatively constant by an anodic depolariser and the increase in E_C can be counteracted by decreasing the total applied potential, E . In practice continuous adjustment of the total applied voltage is necessary to accommodate changes in concentration, over-voltage and iR drop and thereby hold the potential at the cathode at a constant value.

When the electrode potential is controlled such that only a single reaction can occur the current is governed by the rate of diffusion of the reducible ions. The current at

any instant is therefore given by the expression:

$$i_t = -nF \frac{dN}{dt}$$

where dN/dt represents the number of moles that react at the electrode in unit time. When dN/dt is controlled by the rate of diffusion then, from Fick's Law:

$$-dN/dt = D \cdot A \frac{dC}{dx}$$

where D is the diffusion coefficient of the reducible substance (cm^2/sec). A is the electrode area (cm^2) and dC/dx is the concentration gradient at the electrode surface. The instantaneous current is hence given by:

$$i_t = nF D \cdot A \frac{dC}{dx}$$

From Nernst's work the concentration in the thin diffusion layer is virtually a linear function of distance from the electrode when the solution is thoroughly stirred and so

$$\frac{dC}{dx} \approx \frac{C - C_{x=0}}{\sigma}$$

where C is the concentration in the body of the solution, $C_{x=0}$ is the concentration at the electrode surface and σ is the thickness of the diffusion layer. Under experimental conditions $C_{x=0}$ is much smaller than C so that dC/dx is very nearly equal to C/σ and consequently:

$$i_t \approx nF D A C / \sigma$$

The above equation explains why the current is greater when the efficiency of stirring is improved, since the value for σ is decreased by increased stirring.

The current at any instant is also proportional to the concentration and hence to the number of moles of the remaining substance and accordingly:

$$i_t = nF \frac{dN}{dt} = -nF \frac{dN}{dt}$$

$$\frac{DA}{\sigma} \cdot C = - \frac{dN}{dt} = -V \cdot \frac{dC}{dt}$$

$$\frac{DA}{\sigma V} \int_0^t dt = - \int_{C_0}^{C_t} \frac{dC}{C}$$

$$C_t = C_0 e^{-DA t / \sigma V}$$

where V is the solution volume,
and consequently:

$$i_t = i_0 \cdot e^{-DA t / \sigma V} = i_0 \cdot 10^{-0.43 DA t / \sigma V}$$

where C_0 and i_0 are the initial values of the concentrations and current at zero time.

By setting $k = 0.43 DA / \sigma V$ the equation is written:

$$i_t = i_0 \cdot 10^{-kt} \quad (1)$$

From the above equation (1) it can clearly be seen that the electrolysis current decreases exponentially with time to-

wards zero. The time needed to complete an electrolysis diminishes as the value for k increases and since $k = 0.43 \cdot DA/\sigma V$ the aim for controlled potential coulometric analysis should be to increase the area of the electrodes and keep the volume of the solution as small as possible.

From equation (1) it can also be seen that the current approaches zero asymptotically and there is no definite time at which the reaction is said to be completed. In many cases an appreciable background current is observed with the supporting electrolyte alone and in such instances the current decays rather to this background current than to zero. In calculations the background current is considered to be constant during an analysis which means that the background current contributes with a constant increment to the total current. Laitinen⁴ has used the term half-time of electrolysis for calculating the completeness of an electrolysis. This means if $t = t_{1/2}$ when $i/i_0 = 1/2$ we find from the equation that $t_{1/2} = \log 2/k$. Thus for instance if 99.9% electrolysis is desired the electrolysis is stopped after 10 half-times.

It should be noticed that equation (1) does not hold at the beginning of the electrolysis in some cases, because the initial concentration may be so high that the proportionality between current and concentration does not hold and the source is unable to supply the total voltage at the level of current that can be sustained by the mass

transfer rate.

Starting from the above theory for controlled potential coulometry, together with requirements for rapid and accurate analysis, the following conditions are desirable to be fulfilled for the electroactive species involved in order to bring the sample constituent quantitatively to the desirable oxidation state:

- a) The oxidation or reduction must be quantitative.

This means that 100.0% current efficiency must be obtained.

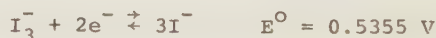
- b) It must be possible to remove the excess oxidant and reductant.

- c) The oxidation or reduction step must be sufficiently selective to avoid interference from other components.

- d) A rapid or relatively rapid electrode reaction is required for the electroactive species.

The iodine-iodide couple fulfills the above features.

According to the relatively low reduction potential:



iodine is quantitatively reduced to iodide by moderately strong reductant and iodide is quantitatively oxidized to iodine by moderately strong oxidants.

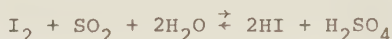
The coulometric analyses involving the iodine-iodide couple fall into two categories. The first comprises procedures

that use iodine for easily oxidized substances. These are termed iodimetric methods. The second method involves analysis of oxidizing agents. The substance that is going to be determined is treated with an excess of iodide ions and the quantity of iodine formed is determined. These are termed iodometric methods. Papers I-V in this thesis are based on controlled potential iodimetric determinations and papers VI-VIII are based on controlled potential iodometric determinations.

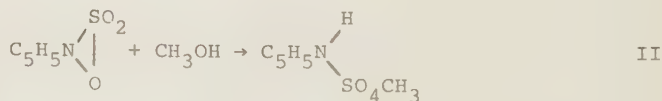
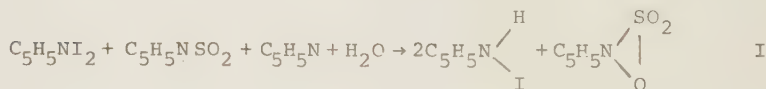
PAPERS I-V: IODIMETRIC DETERMINATIONS.

The determination of water is one of the most common analytical procedures. Because of its wide-spread importance many procedures involving both physical and chemical methods have been developed.

A simple and widely applicable method was described by Karl Fischer⁵ in 1935. It is based on principles originally investigated by Bunsen⁶, who found that the reaction between iodine and sulphur dioxide in a solution of water proceeds as follows:

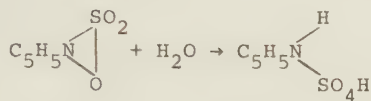


Karl Fischer used anhydrous methanol to dissolve the iodine and sulphur dioxide and added pyridine to displace the equilibrium completely to the right. Smith, Bryant and Mitchell⁷ investigated the stoichiometry of the reaction and showed that both the pyridine and the methanol take part. The reaction was shown to take place in two distinct steps with water involved only in the first step:



Each mole of water thus requires 1 mole of iodine.

In the absence of methanol the following reaction is possible:



so that 2 moles of water react with 1 mole of iodine. However, in the presence of methanol in excess the intermediate compound reacts preferentially with methanol. Numerous preparations of Karl Fischer reagents have been described. For various special purposes the composition may be altered. For example in the determination of water in alcohols the mole ratio pyridine/iodine should not be too high. On the other hand for the determination of water in acetone high concentrations of pyridine may be desirable.

Due to the instability of the Karl Fischer reagent and the high sensitivity for moisture, work in almost closed systems is necessary. As the rapid redox couple iodine-iodide is involved, a coulometric approach with internal generation of iodine in a spent Karl Fischer reagent seems attractive. Such a method was also proposed by Meyer and Boyd⁸, who generated iodine electrolytically in a spent Karl Fischer reagent by constant current coulometry. A coulometric method at controlled potential has been proposed by Lindbeck and Freund⁹. A known excess of iodine to the water in samples was generated followed by a reduction of the remaining iodine.

Papers I-II describe a controlled potential coulometric

method for the determination of water. The intention has been to investigate a rapid and accurate coulometric microdetermination method suitable for a large variety of substances. In paper I the development of an electrolysis cell, a potentiostat and an integrator is described. In construction of the electrolysis cell the following important factors have been considered:

- a) Type of electrodes
- b) Stirring
- c) Volume to electrode area ratio
- d) Cell resistance
- e) Separation of anode and cathode compartments
- f) De-aeration of the cathode compartment

The potentiostat and integrator have been constructed based on principles first devised by Booman¹⁰ and Kelley et al.¹¹ and later modified by Johansson¹² for microanalytical purposes. Modern commercially available components for the electronic circuitry have been used and the circuitry is fitted to the electrolysis cell and chemical system used. The paper describes also the development of a Karl Fischer reagent suitable for micro determination of water in a controlled potential system.

One of the main problems in working with the Karl Fischer reagent is to obtain a proper control of the side-reactions involved with the reagent. There is consequently at every analysis of water a need for a correction factor due to these side-reactions caused by the reagent and further a

correction factor due to the earlier related residual current. However, Figure 1 clearly shows that with the procedures worked out for a determination of water these corrections were wholly under control. Besides the determination of water in organic solvents also water in substances dissolved in organic solvents was analysed. Table I gives the result from the determination of water in some organic peroxides.

TABLE I

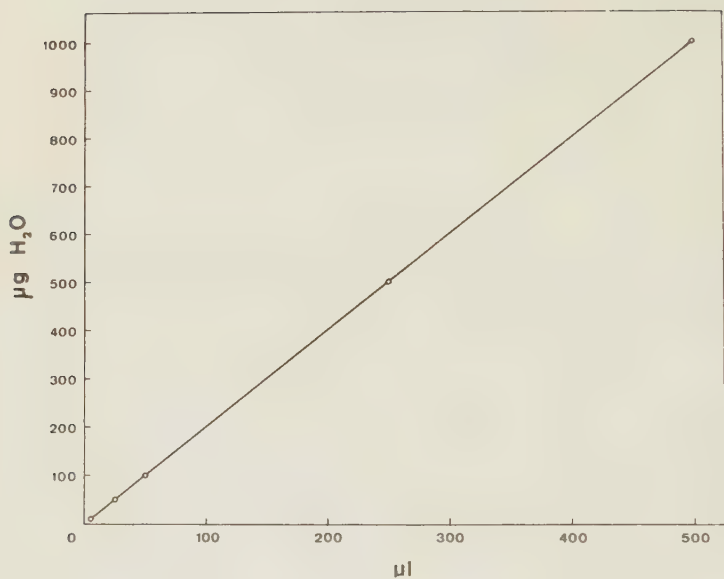
Coulometric determination of water in some organic peroxides.

Name	Formula	Number of determ.	Water found %
t-Butylperoxide *	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	8	0.0331 ± 0.0006
Cumyl peroxide *	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	6	0.348 ± 0.001
Benzoyl peroxide **	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C} \quad \text{C} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	5	0.610 ± 0.001
Lauroyl peroxide ***	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{H}_{23}\text{C}_{11}-\text{C} \quad \text{C}-\text{C}_{11}-\text{H}_{23} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	5	0.032 ± 0.002

* dissolved in anhydrous methanol

** dissolved in a mixture of pyridine and methanol (2:5)

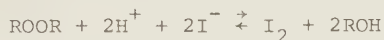
Figure 1



Micrograms of water found vs microliters of sample solution added.

The butyl and cumyl peroxides were determined directly without any interferences.

Because of the reaction:



the benzoyl and lauroyl peroxides were determined in an indirect way. The amount of iodine formed in the above reaction was calculated for the sample containing the benzoyl or lauroyl peroxide using data of purity according to Fiedler¹³. The difference between the calculated value and the value obtained at the determination gave after correction the amount of water in the peroxides.

In paper II the coulometric system has been improved. A better cell geometry and the use of clay filters make it possible to carry out electrolysis with larger currents.

The electronic circuitry was equipped with a booster and a digital read-out, which resulted in capability to supply larger currents and a faster and more accurate presentation, respectively. Hence, the determination range has been extended and the accuracy improved. The apparatus has also been supplied with movable furnace systems which have further extended the range of application.

In the temperature region up to 400°C the furnace was constructed of aluminium and a Pyrex glass tube, in which the samples were inserted. When higher temperatures, up to 1200°C , were needed a small split type furnace was used together with a quartz tube for the samples. The temperatures of the furnaces were controlled within a few degrees by calibrated thermocouples.

Table II gives an example on high temperature analysis (900°C) for the determination of the moisture content in some different types of UO_2 -rods, weighing in the range 11.5 - 14 g each.

TABLE II

Determination of water in UO_2 -rods.

Density of the sample (g/cm^3)	Type A	Type B	Type C
		ppm H_2O	
9.5	90.3	108.3	161.4
10.0	54.6	51.1	96.2
10.1	22.0	20.0	36.6
10.2	13.6	15.8	22.1
10.3	10.2	10.5	11.8
10.4	4.4	6.6	4.9
10.5	3.8	4.7	4.0

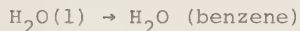
Type A: Stored 24 hours at 50% rel.hum.

Type B: Surface-polished, washed and dried 12 hours in warm air.

Type C: Stored 24 hours at 90% rel.hum.

The low solubility of water in many non-polar organic liquids has caused great problems which can be seen from the relevant literature. Benzene seems to have attracted the greatest interest.

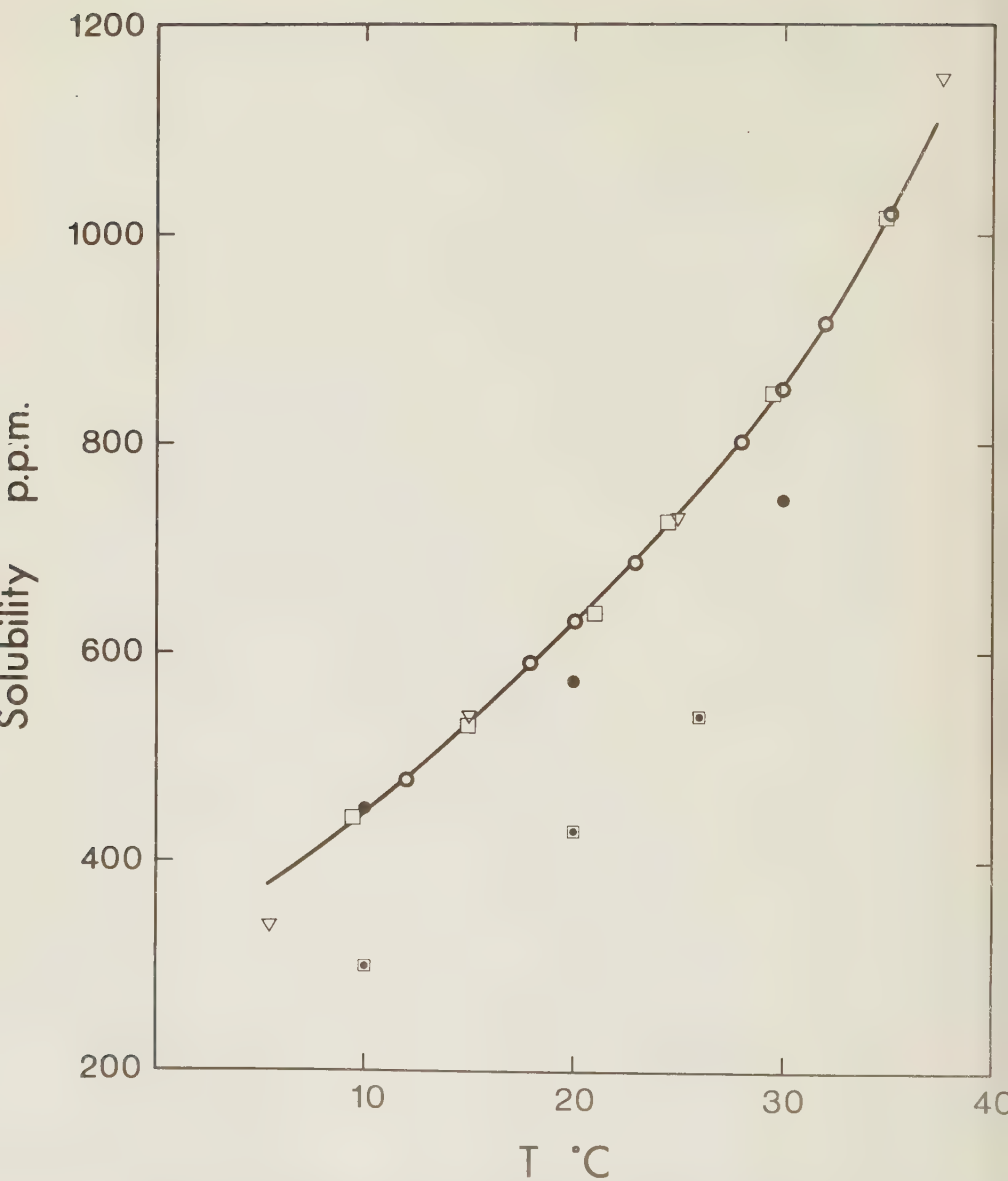
In paper III an investigation concerning the water content in benzene has been performed. Our intention was to perform accurate solubility determinations for water in benzene under controlled conditions. Therefore, we restricted the temperature interval to $25 \pm 10^{\circ}\text{C}$ because results of measurements at 10°C and 40°C showed a significantly lower accuracy than for the results obtained in the interval above. Consequently, when using a larger interval special precautions for control of the experimental conditions must be taken into consideration for obtaining the same high accuracy over the whole interval. Figure 2 shows the results obtained together with some other available literature data. The solubility data obtained were also used for the calculation of ΔH and ΔS for the reaction:



in the measured interval.

Micro-methods for the determination of the carbon and hydrogen content in organic materials have received a great deal of attention during recent years. The basic principles of

Figure 2



Plot of the solubility of water in benzene vs. the temperature in degrees centigrade.

Hill (14) ▽

Moule and Thurstone (16) □

This research ○

Rosenbaum (15) ●

Joris and Taylor (17) ◻

18

Pregl's method still stand and the method is more widely used than any other. The combustion products in the Pregl method are collected in appropriate absorbents and from the increase in weights of the absorbents the carbon and hydrogen are determined. The aim of all commercially available instruments for C-H determination is to avoid the rather time consuming and complicated weighing processes. An excellent review of such instruments is given by Salzer¹⁹.

He presented the following measuring principles for the determination of carbon and hydrogen:

1. Heat conductivity

- a) gas chromatographic separation of the combustion products
- b) separation of the combustion products by absorbents, adsorbents, and by freezing out.

2. Conductometry

3. Coulometry

4. Combination of conductometry and coulometry

5. Colorimetric titration

6. Generation of current in a galvanic cell

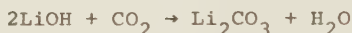
7. Manometric measuring

8. Automatic weighing of the absorption tubes

Among these the coulometric principles in which the carbon and hydrogen in the sample are converted to water seemed most attractive. However, due to the way of determining the water the earlier methods failed in accuracy.

Paper IV describes an accurate method for simultaneous determination of carbon and hydrogen. The method uses the earlier investigated method for the determination of water in solids^{II}. The carbon and hydrogen in a sample are oxidized to carbon dioxide and water, respectively. The water is first trapped while the carbon dioxide passes and is converted by lithium hydroxide to water and coulometrically determined. The retained water is then released and determined in the same way.

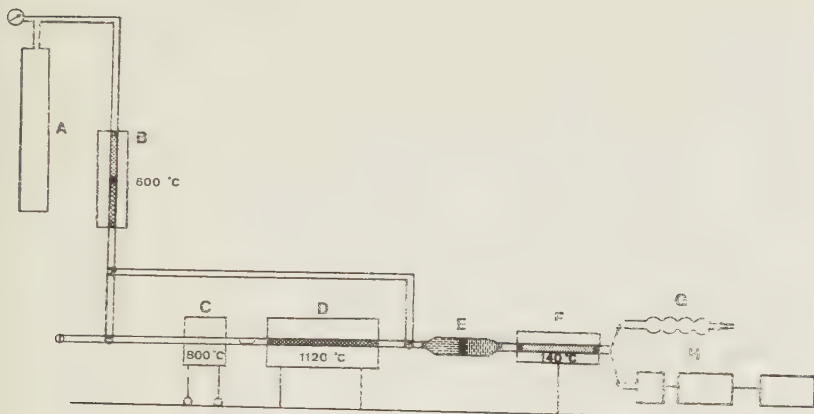
The reaction:



has been studied extensively by the use of a specially built stopcock system. Optimum flow rate and temperature have been determined. A high precision method for the determination of the hydrogen content in a sample separately is given as an application specially useful for purity determinations and for detecting small differences in the composition of a sample.

Among the methods proposed for micro determination of oxygen in organic compounds, the method described by Unterzaucher²⁰ is the most widely used. Figure 3 gives a schematic description of the apparatus. The substance to be examined is decomposed thermally in a stream of nitrogen and the resulting gases are allowed to pass over carbon heated to a constant

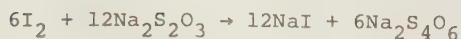
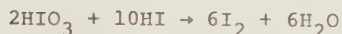
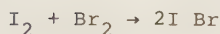
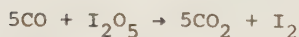
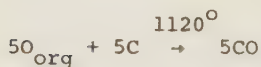
Figure 3



Apparatus for the determination of oxygen.

- A. Nitrogen tank.
- B. Furnace filled with CuO and Cu.
- C. Movable furnace.
- D. Furnace with carbon-filling.
- E. Tube with ascarite and dehydrite.
- F. Oven filled with anhydrous iodic acid.
- G. Collecting tube containing 20% NaOH solution.
- H. Electrolysis cell and coulometric apparatus.

temperature of 1120°C , whereby the oxygen is completely converted into carbon monoxide. After removal of interfering gases the carbon monoxide is caused to react with iodine pentoxide at 140°C and carbon dioxide and iodine are formed. The iodine formed is adsorbed in a dilute sodium hydroxide solution and can be titrated with a thio-sulphate solution directly. However, the conversion factor for this can be increased considerably by a multiplication process in which the iodine is oxidized with bromine to iodic acid, which after destruction of the excess bromine with formic acid is allowed to react with iodide. The iodine so formed is then titrated as above. This multiplication process is generally necessary for accurate titration results, because of the small amounts of iodine released in the micro analyses of oxygen. The reactions involved at a determination of oxygen are the following:

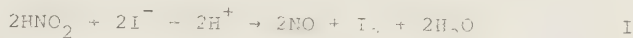


Since iodine has been extensively studied in connection with coulometric measurements we found it attractive to construct a coulometric apparatus for continuous reduction of the iodine formed at the reaction between iodine pentoxide and carbon monoxide. The method described in paper V is based on the principles investigated by Unterzaucher but instead of titrating the iodine released in the final step we use a coulometric reduction of the iodine. All time consuming manual operations have thus been avoided which have led to a more rapid and accurate method. As very small amounts of iodine can be determined coulometrically with high accuracy also submicrogram determinations of oxygen have been possible. The lowest limit depends on the balance used.

With the apparatus described here the pyrolysis process can be followed continuously, which has made it possible to determine the best conditions for the pyrolysis.

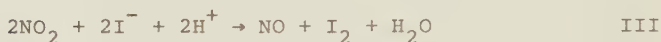
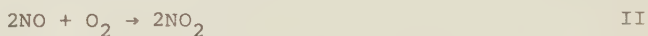
PAPERS VI-VIII: IODOMETRIC DETERMINATIONS.

Already in the beginning of this century iodometric methods^{21,22} were proposed for the determination of nitrite. The reaction:



was used and the iodine formed was titrated with thiosulphate. Despite the fact that the iodometric methods for the determination of nitrite have proved to be superior to other

methods for many applications, their extension has been limited specially for micro determinations. This is due to the difficulty of excluding oxygen, leading to the following reactions:



which will cause too high results.

The coulometric technique we have developed in our earlier papers seems to be very suitable to adapt for an iodometric method for the determination of nitrite. Paper VI describes such a method. The earlier investigated electrolysis cell was supplied with two nitrogen inlets, one ending below the surface of the cell solution and the other above. Hence, the nitric oxide formed in reaction (I) was expelled and any oxygen was prevented from entering the cell.

The method investigated made it possible to determine concentrations of nitrite down to the ppm level with very high accuracy. The intense discussions concerning food additives during recent years, and especially nitrite, led us to apply our method to analyses of nitrite in different kinds of foods such as vegetables and meat-products. The method proved to be almost free from interferences and very little pretreatment of the products to be analysed was needed.

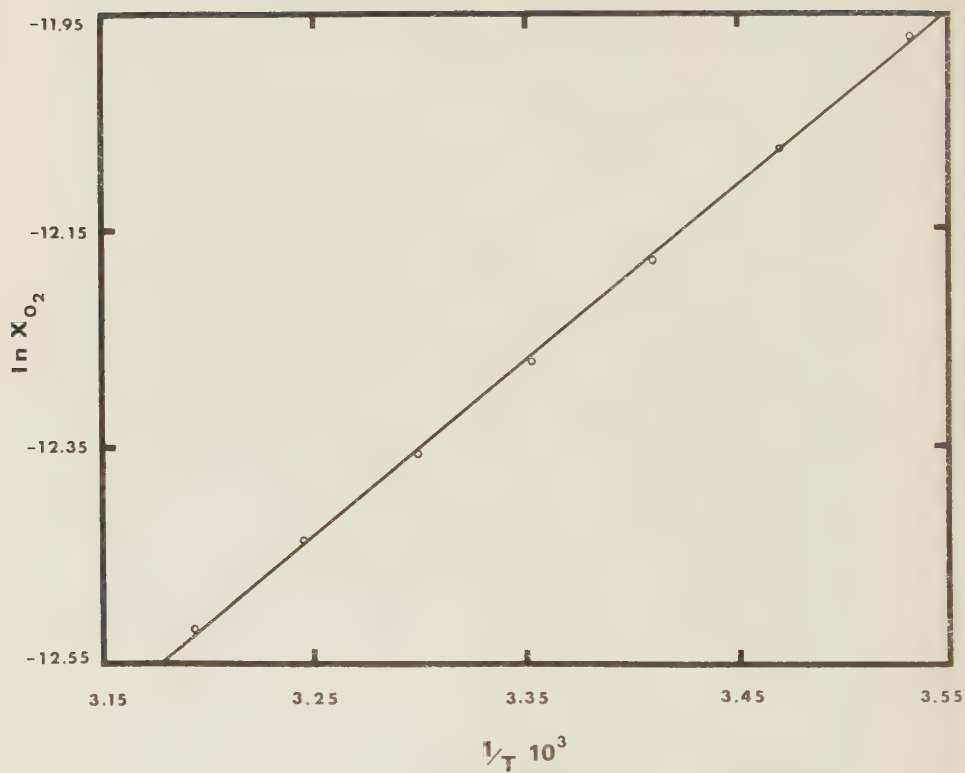
When studying the three reactions involved between iodide and nitrite in the presence of oxygen in the electrolysis cell it seems evident that if only known amounts of oxygen are allowed to enter the cell a reliable method for the determination of oxygen is obtained. Paper VII describes such a method for the determination of oxygen. Iodide is allowed to react with known amounts of nitrite and the nitric oxide so formed will react with any oxygen in the sample added. Due to the low solubility of both oxygen and nitric oxide rather large excess of nitric oxide must be formed to obtain quantitative reaction with all the oxygen added. The literature concerning the solubility of oxygen in water at varying temperatures shows very large discrepancies and since for many purposes it is very important to have correct values we applied our method on the determination of the solubility of oxygen in water at varying temperatures. We worked in the range 10-40°C which seemed to be the most interesting range and performed besides some thermodynamic calculations.

We expressed the solubility of oxygen in water at different temperatures as mole fractions and used the equation:

$$\ln X_{O_2} = - \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S}{R} + \ln p_{O_2}$$

A plot of $\ln X_{O_2}$ vs the reciprocal of the absolute temperature is shown in Figure 4. The ΔH° was determined to -13.40 kJ mol⁻¹ and ΔS° to -134 J mol⁻¹ K⁻¹ from the straight line thus obtained. Table III presents as a comparison some avail-

Figure 4



Logarithm of mole fraction of solubility of oxygen in water vs reciprocal absolute temperature.

able literature data for ΔH° at 25°C .

TABLE III

Some enthalpy values at 25.0°C for the solubility of oxygen in water.

Author	$-\Delta H^\circ$ (kJ mol ⁻¹)
Washburn and Strachan ²³	12.44
Montgomery ²⁴	12.01
Rossini et al. ²⁵	15.9
This research	13.40

In working with the earlier described method for the determination of nitrite^{VI} we have met very often an interest for the determination of nitrate. The existing methods for the determination of nitrate often based on colorimetric procedures are not very specific. However, as a rather specific and wide-spread colorimetric method²⁶ for the determination of nitrite exists many procedures have been proposed for the quantitative reduction of nitrate to nitrite. The use of a coppered cadmium reductor seemed to be the most attractive reduction method for many applications.

A comparison of the reducing efficiency between a cadmium reductor and a coppered cadmium reductor at various pH is shown in Table IV. Samples containing 100 μg of sodium nitrate were allowed to pass the reductors and the eluates were coulometrically analysed. The wash solutions were 2%

ammonium chloride buffers adjusted to the appropriate pH with ammonia and/or hydrochloric acid.

TABLE IV

Effect of pH on the reduction of nitrate to nitrite.

pH of the wash solution	Type of reductor	
	Cu/Cd	Cd
	Nitrate reduced to nitrite %	
9	100	100
7	100	100
5	100	98
3	98	80

Thus we adopted a coppered cadmium reductor to our coulometric nitrite method and worked out the optimum conditions for accurate and rapid conversion of nitrate to nitrite. Paper VIII describes the development of an accurate method for the determinations of nitrate. Tests of different preparations of reductors and the best reductor conditions have been worked out. The method has been applied on a large variety of samples where nitrate alone or mixtures of nitrate and nitrite have occurred.

ACKNOWLEDGEMENTS

I wish to thank Professor K.J. Karrman for his invaluable support and encouragement. I also want to thank Professor Gillis Johansson, who introduced me to the field of electroanalytical chemistry. My thanks are also due to Mr Thorsten Thorneman for skilful mechanical constructions; to Mr Kjell Malm for construction of the electronics; to Mr Alf Lundberg and Mr Siegfried Klein for their glass-blowing and to Mrs Leokadia Postén for help with the literature research. I am also indebted to Dr Lars-Gunnar Torstensson and to all my colleagues at the Analytical Department who have contributed with valuable discussions. I would also like to thank Mrs Britt Johansson and Mrs Lena Andersson for experimental assistance; Mrs Ingrid Norrman for skilful typing of the manuscripts and Dr Peter Sellers for revising the English text. Finally I would like to thank The Swedish Board for Technical Development for financial support during the years 1968-1970.

REFERENCES

1. L. Szebelledy and Z. Somogyi, *Z.Anal.Chem.*, 1938, 112, 313.
2. A. Hickling, *Trans.Faraday Soc.*, 1942, 38, 27.
3. J.J. Lingane, *Electroanalytical Chemistry*, 2d ed., Interscience Publishers Inc., New York, 1958.
4. H.A. Laitinen, *Chemical Analysis*, Mc Graw-Hill Book Co., New York, 1960.
5. K. Fischer, *Angew.Chem.*, 1935, 48, 394.
6. R. Bunsen, *Annalen*, 1853, 86, 265.
7. D.M. Smith, M.D. Bryant and J. Mitchell Jr., *J.Am.Chem. Soc.*, 1939, 61, 2407.
8. A.S. Meyer Jr. and C.M. Boyd, *Anal.Chem.*, 1959, 31, 215.
9. M.R. Lindbeck and H. Freund, *Anal.Chem.*, 1965, 37, 1647.
10. G.L. Booman, *Anal.Chem.*, 1957, 29, 213.
11. M.T. Kelley, H.C. Jones and D.J. Fischer, *Anal.Chem.*, 1959, 31, 488.
12. G. Johansson, *Talanta*, 1965, 12, 163.
13. U. Fiedler, *Talanta*, 1973, 20, 1309.
14. A.E. Hill, *J.Am.Chem.Soc.*, 1923, 45, 1143.
15. C.K. Rosenbaum and J.H. Walton, *J.Am.Chem.Soc.*, 1930, 52, 3568.
16. D.C. Moule and W.M. Thurston, *Can.J.Chem.*, 1966, 44, 1361.
17. G.G. Joris and H.S. Taylor, *J.Chem.Phys.*, 1948, 16, 45.
18. F. Pregl, *Quantitative Organic Microanalysis*, 3rd English ed., Blakiston, Philadelphia, 1937; *ibid.*, 4th English ed., Blakiston, Philadelphia, 1946.

19. F. Salzer, *Microchem.J.*, 1971, 16, 145.
20. J. Unterzaucher, *Analyst*, 1952, 77, 584.
21. B.S. Davisson, *J.Am.Chem.Soc.*, 1910, 38, 1683.
22. C.A. Abeledo and I.M. Kolthoff, *J.Am.Chem.Soc.*, 1931, 53, 2893.
23. E.W. Washburn and E.K. Strachan, *J.Am.Chem.Soc.*, 1913, 35, 681.
24. H.A. Montgomery, N.S. Thom and A. Cockburn, *J.Appl.Chem.*, 1964, 14, 280.
25. F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, 1952.
26. J.P. Griess, *Chem.Ber.*, 1879, 12, 426.

SIGMA · TRYCK
TLTH · Lund

